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Rubber-Reinforcing Polyester Fiber

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(54) Title of the Invention: **Rubber-Reinforcing Polyester Fiber**

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SPECIFICATION

1. Title of the Invention

Rubber-Reinforcing Polyester Fiber

2. Claims

(1) A rubber-reinforcing polyester fiber comprising a polyester that uses as polymerization catalysts 30 to 150 ppm of an antimony compound in terms of antimony and 5 to 120 ppm of a germanium compound in terms of germanium, and that has the following properties.

- A. Carboxyl end group (COOH) content: $\text{COOH} \leq 25 \text{ eg}^1/\text{ton}$
- B. Diethylene glycol (DEG) content: $\text{DEG} \leq 1.3 \text{ wt } \%$
- C. Intrinsic viscosity (IV): $\text{IV} \geq 0.85$
- D. Dimensional stability (intermediate elongation + dry heat shrinkage) (S):
 $S \leq 12.0\%$
- E. Terminal modulus (M_t): $M_t \leq 50 \text{ (g/d)}$

(2) The rubber-reinforcing polyester fiber according to Claim 1, wherein the number of foreign substances in a yarn as measured with an optical microscope using transmitted light is 800 per milligram or less.

(3) The rubber-reinforcing polyester fiber according to Claim 1, wherein the fiber toughness ($T \sqrt{E}$) and dimensional stability (S) satisfy the expression (I) below.

$$T \sqrt{E} \geq S + 22.0. \quad (\text{I})$$

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a rubber-reinforcing polyester fiber. More specifically, the present invention relates to a rubber-reinforcing polyester fiber that has good dimensional stability, high strength, and exceptional durability.

¹ Translator's note: Possible misprint for "eq."

(Prior Art)

Polyester fibers have exceptional mechanical properties, dimensional stability, and durability, and are widely used in industrial applications as well as in apparel. These fibers are extensively used in tire cords and other rubber material-reinforcing applications, as these characteristics are utilized therein. In the past, high-strength original yarns formed by stretching low-oriented unstretched yarns at a high ratio have been used in tire cord applications. In recent years, however, original yarns obtained by stretching relatively highly oriented unstretched yarns (so-called partially oriented yarns ("POY")) have come into use. This technique was developed in response to demands for better dimensional stability in the cords and for enhanced tire performance, and especially uniformity, despite a certain degree of strength being sacrificed.

However, tire cords having high strength and high toughness that still retain their dimensional stability have increasingly been required in recent years in order to improve tire performance. An example of a response to such requirements is disclosed in Japanese Patent Application (Kokai) Laid Open No. 60-88120, in which a POY is stretched at a low speed. However, the disclosed stretching technique provides only a minor range of improvement in the toughness (product of strength and elongation) of the fiber itself, meaning that the strength of tire cords in which the fiber is employed will not see any significant improvement, and the required level of strength and toughness will be insufficient. Reducing defects in the fiber is thought to be effective in improving toughness. In other words, various defects (foreign substances) present in tire cords are primarily caused by particles present in the polymer. These particles are often derived from polymerization catalysts, and it is accordingly of primary necessity to eliminate them.

Examples of catalysts used to manufacture rubber-reinforcing polyester fibers include manganese acetate, antimony trioxide, and phosphoric acid catalyst systems, which are disclosed in Japanese Examined Patent Application Publication (Kokoku) No. 37-5821; calcium acetate, antimony trioxide, and phosphorous acid systems, which are disclosed in Japanese Patent Application (Kokai) Laid Open No. 55-12871; and lithium acetate, antimony trioxide, and phosphorous acid systems, which are disclosed in Japanese Patent Application (Kokai) Laid Open No. 51-134789. Using these catalysts in polymerization will generate numerous catalyst-

derived particles and create defects in the fiber. Accordingly, it will be impossible to satisfy the levels of high strength and toughness as required in the latest fibers.

(Problems That the Invention Is Intended to Solve)

The present inventors conducted diligent investigations on polymers that can yield polyester fibers having good dimensional stability and exceptional strength and toughness, and arrived at a rubber-reinforcing polyester fiber that has high toughness as well as good dimensional stability, heat-resistance, and durability.

(Means Used to Solve the Above-Mentioned Problems)

The aforementioned object of the present invention can be achieved by means of a rubber-reinforced polyester fiber comprising a polyester that uses as polymerization catalysts 30 to 150 ppm of an antimony compound in terms of antimony and 5 to 120 ppm of a germanium compound in terms of germanium, and that has the following properties.

- A. Carboxyl end group (COOH) content: $\text{COOH} \leq 25 \text{ eg/ton}$
- B. Diethylene glycol (DEG) content: $\text{DEG} \leq 1.3 \text{ wt } \%$
- C. Intrinsic viscosity (IV): $\text{IV} \geq 0.85$
- D. Dimensional stability (intermediate elongation + dry heat shrinkage) (S):
 $S \leq 12.0\%$
- E. Terminal modulus (M_t): $M_t \leq 50 \text{ (g/d)}$

The polyester of the present invention refers to a polyester in which ethylene terephthalate is the principal repeating unit. To improve dimensional stability and strength, the polyester used is preferably a polyethylene terephthalate that does not have any added or copolymerized third components other than diethylene glycol byproducts, and contains essentially no inorganic particles or other additives.

The present inventors conducted diligent investigations into factors that reduce the strength of the fibers, in order to increase their strength and toughness while retaining their good dimensional stability. As a result, the inventors identified the yarn defects, and in particular the catalyst-derived particles, that have prevented fibers from having increased strength. The

inventors further discovered that among these particles, the metallic antimony formed from the reduction of antimony compounds used as a polymerization catalyst imparts an adverse effect on strength and toughness. In view of this, the inventors conducted diligent investigations into reducing the amount of metallic antimony, and as a result of which discovered that the joint use of an antimony compound and a germanium compound as polymerization catalysts could reduce the content of foreign substances without altering the content of carboxyl end groups or diethylene glycol, or hindering other properties of the polymer.

Accordingly, in the present invention, an antimony compound and a germanium compound must be used jointly as polymerization catalysts. There is a limit to the extent the content of the antimony compound, when used alone, can be reduced in order to obtain a polymer of a desired IV within a normal polycondensation time; consequently, there is a limit to the extent the content of metallic antimony itself can be reduced. Using the germanium compound alone will increase the diethylene glycol content and will degrade the dimensional stability of the yarn. Examples of antimony compounds that are preferably used as polymerization catalysts include antimony trioxide and antimony pentoxide, while germanium dioxide is preferably used as the germanium compound. The amount of antimony compound contained in the polyester fiber of the present invention must be 30 to 150 ppm. If the amount of the antimony compound is less than 30 ppm, the amount of the germanium compound used jointly in order to preserve the polymerization reactivity will need to be increased, thereby causing costs to increase together with the diethylene glycol content, which in turn will reduce dimensional stability. If the amount of antimony compound exceeds 150 ppm, the combined use of the germanium compound will be rendered ineffective in reducing the content of the metallic antimony, and any improvement in the strength and toughness of the yarn will not be realized. On the other hand, the amount of the germanium compound must be 5 to 120 ppm. If the amount of the germanium compound is less than 5 ppm, it will be impossible to establish a level of 150 ppm or less for the antimony content of the antimony compound used in order to preserve the polymerization reactivity. If the germanium content of the germanium compound exceeds 120 ppm, manufacturing costs will dramatically increase, as will the diethylene glycol content, which in turn will reduce dimensional stability. From the above perspective, the antimony content of the antimony compound is preferably 40 to 120 ppm, and ideally 80 to 120 ppm, while the amount of germanium compound is preferably 5 to 80 ppm, and ideally 6 to 30 ppm.

The polymer of the present invention is obtained either by a direct polymerization method, or a so-called DMT method, in which dimethyl terephthalate is employed. When the DMT method is used, a manganese compound is preferably used as the transesterification catalyst therefor. Lithium compounds, magnesium compounds, or the like cause particles to form in the polyester and are accordingly not preferably used.

The carboxyl end group (COOH) content in the polyester fiber of the present invention must be 25 eg/ton or less. If the COOH content exceeds 25 eg/ton, the fiber will quickly deteriorate within the rubber and prove insufficiently durable as a rubber-reinforcing material. From the above perspective, the COOH group content is preferably 21 eg/ton or less.

The diethylene glycol (DEG) content in the polyester fiber of the present invention must be 1.3 wt % or less. If the DEG content exceeds 1.3 wt %, the dimensional stability of the fiber will be poor, and its ability to resist heat in the rubber will be reduced. From the above perspective, the DEG content is preferably 1.1 wt % or less.

The intrinsic viscosity (IV) of the polyester fiber of the present invention must be 0.85 or greater. If the IV is less than 0.85, the fatigue resistance of the fiber will be poor, rendering the fiber unusable as a rubber-reinforcing material. From the above perspective, the IV is preferably 0.9 or greater. However, the IV is preferably 1.3 or less in terms of fiber spinnability and other operational aspects, such as stability.

The dimensional stability (intermediate elongation + dry heat shrinkage) of the polyester fiber of the present invention must be 12% or less. If the dimensional stability exceeds 12%, poor dimensional stability of the cord will result when used in molding tires, and the uniformity of the tire will be lowered. From the above perspective, the dimensional stability is preferably 10% or less. However, the dimensional stability is preferably 8% or more because of considerations related to the ease of manufacture.

The terminal modulus of the polyester fiber of the present invention must be 50 g/d or less. If the terminal modulus exceeds 50 g/d, the fiber will have low tenacity when twisted, rendering any increase the tire cord strength impossible, even if the strength of the original yarn

has been increased. From the above perspective, the terminal modulus is preferably 35 g/d or less.

As has been described in the foregoing, the production of catalyst-derived particles can be controlled by jointly using an antimony compound and a germanium compound as polymerization catalysts, and by strictly controlling the amounts thereof. Moreover, the resulting polymer will have a satisfactory COOH content, DEG content, and other polymer properties. It is only when such a polymer is used that polyester fibers that exhibit unprecedentedly high levels of performance can be manufactured.

In other words, and as has been described in the foregoing, minimizing the amount of antimony metal formed from the reduction of the antimony compound used as a polymerization catalyst to as great an extent as possible in the present invention is crucial in order to obtain the high-toughness, satisfactorily durable rubber-reinforcing polyester fiber that is the object of the present invention.

According to the research conducted by the present inventors, the amount of antimony metal formed from the reduction of the antimony compound used as a polymerization catalyst is preferably established at 5 ppm or less in order to achieve further improvement in durability and toughness, with an amount of 3 ppm or less being ideal. The polymerization conditions (time and temperature) are preferably strictly controlled in order to reduce the content of antimony metal. It is also preferable to ensure to as great an extent as possible that no abnormal residence zones are present during spinning, and that all piping and packing components are plated with chromium, coated with Teflon, or otherwise treated in order to control the reduction reaction. Rubber-reinforcing materials such as tire cords require improved toughness along with consistently good dimensional stability (i.e., a consistently low intermediate elongation + dry heat shrinkage value).

The present inventors also conducted diligent investigations into such requirements, and as a result discovered that strictly controlling the amount, type, and addition method of the phosphorus compound used in polymerization is crucial in meeting the aforementioned requirements. Phosphorus compounds are generally used to improve the heat resistance of the polymer; however, as a result of their research, the present inventors quite unexpectedly made

the novel discovery that the phosphorus compounds affect the relation between the dimensional stability and toughness of the fiber, as has been described in the foregoing.

As a result of their research, the present inventors discovered that it is preferable for phosphoric acid to be used as the phosphorus compound, for the residual amount of this compound to be 10 to 40 ppm in terms of elemental phosphorus, and for the phosphorus compound to be added at the start of polycondensation. Controlling the phosphorus compound in such a manner will enable the toughness of the fiber to be raised at the same level of dimensional stability. In other words, the aforementioned conditions are preferred because higher fiber toughness can be obtained even when the dimensional stability is the same, such as when the following equation is satisfied:

$$\text{Strength-elongation product } (T \sqrt{E}) \geq (\text{intermediate elongation} + \text{dry heat shrinkage}) + 22.0.$$

Although the cause behind the effect of the phosphorus compounds remains uncertain, the present inventors have presumed that the formation of the fiber structure during spinning is controlled by the viscosity-enhancing effect of phosphoric acid or other trifunctional phosphorus compounds. Improvements in fatigue resistance that are significantly higher than seen conventionally can be achieved by using a polyester fiber that satisfies the equation $T\sqrt{E} \geq S + 22.0$, as has been described in the foregoing.

The polyester fiber of the present invention can be manufactured specifically according to the following method.

A polycondensation reaction is conducted while jointly using an antimony compound and a germanium compound as polymerization catalysts. In the reaction, it is preferable to use phosphoric acid as the phosphorus compound, and to add the phosphoric acid at the start of polycondensation, before the antimony compound and germanium compound are added. With such polycondensation, polyethylene terephthalate chips (IV of 0.65 or greater; COOH group content ≤ 26 eg/ton; DEG content ≤ 1.3 wt %) will be obtained by suitably selecting the amounts of the components introduced, the temperature of polymerization, and time of polymerization.

The resulting chips are subjected to solid-phase polymerization in accordance with a known method to yield polyethylene terephthalate (IV or 1.0 or greater, and COOH group content ≤ 16 eg/ton), which is slowly cooled in the heating zone after being melt-spun. The yarn is subsequently taken up while being cooled and solidified in a chimney air current. The piping and packing components in the spinning machine are preferably plated with chromium so as to inhibit precipitation (reduction) of the antimony metal. Nonwoven fabric with metal wire (SUS), fashioned to an absolute filtering diameter not larger than $30\text{ }\mu\text{m}$, is preferably used for filtration. It is also preferable to minimize the amount of dust in the nitrogen used in solid-phase polymerization and in the nitrogen used in the spinning machine, and to reduce the dust content by filtering the air used for the chimney air current. The quantity of foreign substances produced in the yarn in the aforementioned yarn-forming method will be kept to a level of 800/mg or less, and preferably 500/mg or less. This method is preferred because improved toughness and durability are obtained at these levels.

High-orientation spinning is performed, and the yarn discharged from the spinneret is taken up at a rate of 1000 m/min, and preferably between 2000 and 4000 m/min inclusive. The unstretched yarn is spun, and then stretched on hot rollers for heat setting at a temperature of 220°C or higher, either directly thereafter or after having being wound once. A terminal modulus of 50 g/d or less can be obtained by suitably stabilizing the draw ratio and relaxation rate in this process.

(Working Examples)

The present invention shall be described in further detail below using working examples.

The properties of the working examples were measured according to the following methods.

- A. The amounts of metal (e.g., antimony, germanium, and phosphorus) in the polymer and fiber were determined by X-ray fluorescence analysis.

B. Carboxyl end group (COOH) content

A 0.5 g sample was dissolved in 10 mL *o*-cresol, and cooled after having completely dissolved. 3 mL chloroform was then added into the resulting solution, and potentiometric titration was performed using a methanol solution of NaOH.

C. DEG content

Gas chromatography was used after the sample had been subjected to alkalinolysis.

D. Degree of elongation, intermediate elongation, and terminal modulus

A Tensilon tensile tester (Toyo Baldwin) was used to determine the S-S curve at a sample length of 25 cm and a take-up rate of 30 cm/min, and to compute the degree of elongation.

The intermediate elongation was determined from the same S-S curve by reading the elongation corresponding to a strength of 4.5 g/d. The terminal modulus was determined by means of obtaining the difference between the breaking stress and the stress taken at the point where the elongation at break had been reduced by 2.4%, and dividing the difference by 2.4×10^{-2} .

E. Dry heat shrinkage (ΔS_d)

A sample in the form of a hank was left for 24 hours or more in an air-conditioned chamber in conditions of 20°C and 65% RH, after which the length of the sample (l_0) was measured under a load that corresponded to 0.1 g/d of the sample. The sample was then left for 15 min in an oven that had been heated to 150°C, in a non-tensioned state. The sample was then removed from the oven and again left for four hours in the aforementioned air-conditioned chamber, after which its length (l_1) was again measured under the aforementioned load. The dry heat shrinkage (ΔS_d) was calculated according to the following equation:

$$\Delta S_d = (l_0 - l_1) / l_0 \times 100 (\%)$$

F. Number of foreign substances in yarn

The sample was separated into single filaments (length: 6 cm) and pulled completely taut on a glass slide to be used for sampling. The number of foreign substances in the yarns was counted by the phase contrast method using an optical microscope (Olympus Optical Co., Ltd.) to scan the sample at a 200-times magnification. The measurements were performed 5 times to determine the mean value X (substances per 6 cm), which was converted into the number of foreign substances per milligram.

G. Intrinsic viscosity (IV)

0.8 g of sample was dissolved in 10 mL *o*-chlorophenol ("OCP" hereunder) at a temperature of 25°C, after which an Ostwald viscometer was used to determine the relative viscosity ($\eta\gamma$) based on the following equation, and subsequently the IV.

$$\eta\gamma = \eta/\eta_0 = t \times d/t_0 \times d_0$$

$$IV = 0.0242\eta\gamma + 0.2634$$

η : viscosity of polymer solution

η_0 : viscosity of solvent

t : solvent falling time (sec)

d : density of solution (g/cm³)

t_0 : OCP falling time (sec)

d_0 : density of OCP (g/cm³)

H. Amount of antimony metal

40 g of polymer was dissolved in 500 mL *o*-chlorophenol (OCP), and the resulting solution was centrifuged (12,000 rpm × 2 hr). The separated products were washed and dried. The spectra of the centrifugally settled particles were measured using an X-ray diffraction device, and used to determine the amount of metallic antimony.

I. Heat resistance in rubber

Cords were embedded in rubber and vulcanized for 6 hr at 150°C. The heat resistance was evaluated according to the tenacity rate. The tenacity rate was graded as "1" (70% or better); "2" (60 to 70%); and "3" (less than 60%).

J. Fatigue resistance (GY fatigue life)

The tube burst time was determined according to ASTM – D885, with an internal tube pressure of 3.5 kg/cm², a rate of rotation of 850 rpm, and a tube angle of 90°. The results are shown as follows.

- "1" At least 30% better than a conventional product (commercial tire cord model 1000-240-703M; Toray Industries, Inc.)
- "2" 10 to 30% better than the conventional product.
- "3" The same level as the conventional product

(Working Example 1)

0.035 parts manganese acetate tetrahydrate was added to 100 parts dimethyl terephthalate and 50.2 parts ethylene glycol, and the resulting mixture was subjected to transesterification according to a normal method. 0.009 parts phosphoric acid (29 ppm in terms of phosphorus) was added to the resulting product, after which 0.0025 parts germanium dioxide (17 ppm in terms of germanium) was added, and then 0.0125 parts antimony trioxide (104 ppm in terms of antimony) was further added. The resulting mixture was subjected to a polycondensation reaction for three hours and ten minutes (final polymerization temperature: 285°C).

The intrinsic viscosity (IV) of the resulting polymer was 0.72, the carboxyl end group ([COOH]) content was 17.1 eg/ton, and the DEG content was 0.7 wt %. The resulting polymer had an antimony content of 100 ppm, a germanium content of 10 ppm, and a phosphorus content of 20 ppm. 0.3 ppm antimony metal was present in the polymer.

The aforementioned polymer was pre-dried for 5 hrs at 160°C, and then subjected to solid-phase polymerization at a temperature of 225°C, resulting in solid-phase polymer chips having an IV of 1.35.

The chips were spun at a spinning temperature of 295°C using an extruder-type spinning machine. During the spinning, a nonwoven metal fabric having an absolute filtration diameter of 15 μm was used as a filter, and the spinneret had round orifices with a diameter of 0.6 mm. The polymer piping and regions of the packing components that would come into contact with the polymer were plated with chromium, and the nitrogen used in the chimney was filtered with a 1- μm filter. The yarns discharged from the spinneret were slowly cooled in a heating cylinder that had been heated to a temperature of 300°C and had a length of 25 cm and an inside diameter of 25 cm. The yarns were subsequently cooled and solidified in the chimney under a cooling current, oiled, and then taken up at the rates shown in Table 1. The ratios and relaxation rates of the resulting unstretched yarns were varied under a stretching temperature of 90°C and a heat treatment temperature of 240°C, to yield stretched yarns.

The resulting polyester fiber yarns contained 150 to 450 foreign substances per milligram, and had intrinsic viscosities of 0.98 to 1.01, a carboxyl end group content of 14 eg/ton, and a DEG content of 0.7 wt%.

Next, preliminary twists of 49 T/10 cm were applied to the stretched yarns in the S direction, and final twists of 49 T/10 cm were then applied in the Z direction, to obtain green cords.

These cords were dipped in an adhesive using a Computreater (C. A. Litzler Co., Inc.) to form treated tire cords. The treatment conditions were: 160°C for a length fixing treatment in the drying unit; 240°C for a tension treatment in the heat treatment unit; and 240°C for a relaxation treatment in the post-treatment unit. The intermediate elongation of the treated cords was brought to 3 to 4% by adjusting the tensioning and relaxation rates. The properties of the original yarns, green cords, and treated cords are shown in Table 1.

Table 1

| No. | Take-up rate (m/min) | Original yarn | | | | | | | Green cord | Treated cord | | Tire |
|-----|-------------------------|-------------------|-------------------|--------------------------------|----------------------|------------------------------|---------------------------|---|-------------------|-------------------|-------------------|-------------------------|
| | | Strength (g/d) | Elongation (%) | Intermediate elongation (%) | Dry shrinkage (%) | Dimensional stability (%) | Terminal modulus (g/d) | Strength-elongation product ($T \sqrt{E}$) | Strength (g/d) | Strength (g/d) | Elongation (%) | Uniformity ² |
| 1 | 500 | 10.9 | 10.7 | 3.5 | 10.2 | 13.7 | 47.7 | 35.7 | 7.21 | 6.95 | 13.7 | P |
| 2 | 1000 | 10.2 | 11.7 | 3.9 | 8.0 | 11.9 | 39.5 | 34.9 | 7.44 | 7.10 | 13.1 | G |
| 3 | 2000 | 9.2 | 13.7 | 6.8 | 2.7 | 9.5 | 30.1 | 34.1 | 7.29 | 7.05 | 12.7 | G |
| 4 | 2500 | 9.0 | 13.1 | 6.6 | 2.3 | 8.9 | 29.7 | 32.5 | 7.34 | 7.15 | 12.5 | G |
| 5 | 2000 | 9.92 | 11.6 | 5.9 | 3.2 | 9.1 | 70.1 | 33.7 | 7.01 | 6.35 | 10.2 | — |

As is clear from the data in Table 1, a high toughness original yarn that exceeds the strength-elongation product stipulated in the present invention (i.e., a high-toughness yarn that satisfies $T \sqrt{E} \geq S + 22.0$) is obtained by using a specific polymer and adopting strict yarn-forming conditions.

However, tire uniformity was unsatisfactory in no. 1, which had a low take-up speed and a dimensional stability in excess of 12. Furthermore, no. 5, which had been spun under the same conditions as no. 3, except that the stretching conditions had been changed and the terminal modulus exceeded 50, showed diminished strength during twisting and dipping despite the high strength-elongation product of the original yarn, and the toughness of the treated cord decreased to a level that was not substantially different from conventional levels. Only fiber nos. 2 through 4 showed sufficiently high toughness and good tire uniformity to fall within the range of the present invention.

² Translator's note: no description is made anywhere in the text of how tire uniformity is graded. The ranking of "G" (good) and "P" (poor) have been used in the table because there are only two levels of uniformity, and because the two symbols are normally used in Japanese with similar denotations.

Working Example 2

Unstretched yarns were obtained using the same polymer that was used in Working Example 1 and under the same conditions used for no. 3 in Working Example 1, but varying the spinning temperature and residence time as well as the carboxyl end group content. As is clear from the data in Table 2, the heat resistance in the rubber decreased when the carboxyl end group content reached 25 eg/ton or more.

Table 2

| No. | COOH content | Heat resistance in rubber |
|-----|--------------|---------------------------|
| 3 | 14 | 1 |
| 6 | 21 | 2 |
| 7 | 28 | 3 |

The amount of diethylene glycol added when the polymer in Working Example 1 was manufactured was varied.

Table 3

| No. | DEG (wt %) | Dimensional stability (S) | Heat resistance in rubber |
|-----|------------|---------------------------|---------------------------|
| 3 | 0.7 | 9.5 | 1 |
| 8 | 1.2 | 9.9 | 2 |
| 9 | 1.5 | 10.5 | 3 |
| 10 | 1.7 | 10.7 | 3 |

As can be seen from the data in Table 3, when the amount of DEG exceeded 1.3 wt %, the dimensional stability suffered and the heat resistance in the rubber declined.

Working Example 3

Chips with an IV of 0.7 were obtained by varying the amount of antimony trioxide and germanium dioxide added during the manufacturing of the polymer in Working Example 1. Polyester fibers were obtained from these chips according to experiment no. 3 in Working Example 1. The results are combined with the polymer properties, and shown in Table 4.

Table 4

| No. | Amount added | | | | COOH (eg/ton) | DEG (wt %) | Sb metal (ppm) |
|-----|--------------------------------|------------------|-------------|-----|------------------|---------------|----------------------|
| | Weight parts | | Metal (ppm) | | | | |
| | Sb ₂ O ₃ | GeO ₂ | Sb | Ge | | | |
| 11 | 0.021 | 0.0025 | 175 | 17 | 17.4 | 0.7 | 7 |
| 12 | 0.016 | 0.0025 | 134 | 17 | 19.4 | 0.7 | 0.8 |
| 13 | 0.005 | 0.013 | 42 | 90 | 20.0 | 0.75 | 0 |
| 14 | 0.003 | 0.016 | 25 | 111 | 28.5 | 1.15 | 0 |
| 15 | 0.003 | 0.026 | 25 | 180 | 20.2 | 1.54 | 0 |
| 16 | 0.016 | 0.0005 | 134 | 3.5 | 29.6 | 0.7 | 4.5 |
| 17 | 0.021 | 0.0005 | 175 | 3.5 | 18.4 | 0.7 | 8 |
| 3 | 0.0125 | 0.0025 | 104 | 17 | 17.1 | 0.7 | 0.3 |

Table 5

| No. | Strength (g/d) | Elongation (%) | Intermediate elongation (%) | Dry shrinkage (%) | Intermediate elongation + dry shrinkage (%) | $(T\sqrt{E})$ | Number of foreign substances in yarn (/mg) | Heat resistance in rubber |
|-----|-------------------|-------------------|-----------------------------------|-------------------------|---|---------------|--|---------------------------------|
| 11 | 8.0 | 13.7 | 6.8 | 2.6 | 9.4 | 29.6 | 3,415 | 1 |
| 12 | 8.8 | 13.5 | 6.9 | 2.7 | 9.6 | 32.3 | 720 | 2 |
| 13 | 9.1 | 14.0 | 6.8 | 2.6 | 9.4 | 34.0 | 300 | 2 |
| 14 | 9.4 | 13.0 | 6.7 | 3.2 | 9.9 | 33.9 | 150 | 3 |
| 15 | 9.3 | 13.5 | 6.8 | 3.5 | 10.3 | 34.2 | 100 | 3 |
| 16 | 8.7 | 13.6 | 6.7 | 2.7 | 9.4 | 32.0 | 750 | 3 |
| 17 | 8.1 | 12.5 | 6.8 | 2.6 | 9.4 | 28.6 | 4,215 | 2 |
| 3 | 9.2 | 13.7 | 6.8 | 2.7 | 9.5 | 34.1 | 320 | 1 |

As is evident from the data in Table 4, Nos. 11 and 17, in which the amount of antimony exceeded 150 ppm, had a high Sb metal content and a large number of foreign substances, leading to a significant decrease in toughness. No. 14, in which the amount of antimony was less than 30 ppm, had a germanium content of 111 ppm; therefore, the polymerization time increased due to the poor polymerization reactivity and an IV of 0.7, and the COOH content increased. Accordingly, the COOH content in the yarn reached 28.5 eg/ton, and the heat resistance in the rubber was insufficient. On the other hand, no. 15, in which a large quantity (180 ppm) of germanium was added in correspondence with less than 30 ppm of antimony, showed an increased DEG content and insufficient heat resistance in the rubber. No. 16, which had less than

5 ppm of germanium, showed an increased COOH content and poor polymerization reactivity when the antimony content was 150 ppm or less. Accordingly, 29.6 eg/ton COOH was present in the yarn, causing the heat resistance in the rubber to be insufficient.

Only nos. 12 and 13, which contained as polymerization catalysts an antimony compound with an antimony content of 30 to 150 ppm and a germanium compound with a germanium content of 5 to 120 ppm, fulfilled the object of the present invention.

Working Example 4

A polymer was obtained according to the same method followed in Working Example 1, with the exception that trimethyl phosphate was used instead of phosphoric acid as the phosphorus component in the polycondensation reaction, but in the same molar amount. The polymer was spun and stretched according to the same method followed for no. 3 in Working Example 1, to obtain stretched yarns that had the properties shown in Table 6.

Table 6

| No. | Strength (g/d) | Elongation (%) | Intermediate elongation (%) | Dry shrinkage (%) | Intermediate elongation + dry shrinkage (%) | $(T\sqrt{E})$ | Intermediate elongation + dry shrinkage + 22.0 | Fatigue resistance |
|-----|-------------------|-------------------|-----------------------------------|-------------------------|---|---------------|--|-----------------------|
| 18 | 9.0 | 13.0 | 6.9 | 3.8 | 10.7 | 32.4 | 32.6 ³ | 2 |
| 3 | 9.2 | 13.7 | 6.8 | 2.7 | 9.5 | 34.1 | 31.5 | 1 |

As can be seen from the data in Table 6, varying the type of phosphorus caused the shrinkage rate to increase by approximately 1% when spinning was performed under the same conditions. As with no. 3, the resulting yarn had high toughness, but when the toughness values of both were compared with regard to the same dimensional stability (intermediate elongation + dry heat shrinkage), the resulting yarn had a lower toughness (i.e., the relation $T\sqrt{E} \geq \text{intermediate elongation} + \text{dry heat shrinkage} + 22.0$ was not satisfied). The fatigue resistance values for nos. 3 and 18 were both superior to conventional yarns, with no. 3, which satisfied $T\sqrt{E} \geq S + 22.0$, being superior to no. 18.

³ Translators' note: this is presumably a typographical error for "32.7"

Working Example 5

A common spinning machine with common packing components was used to spin yarns under the same conditions as no. 3 in Working Example 1, but the filter was not used.

Nor were any special provisions made with regard to filtering or otherwise processing the nitrogen. The values of the properties are as shown below.

Table 7

| No. | Strength (D/d) | Elongation (%) | $T\sqrt{E}$ | Number of foreign substances |
|-----|-------------------|-------------------|-------------|------------------------------------|
| 19 | 8.8 | 12.5 | 31.1 | 910 |
| 3 | 9.2 | 13.7 | 34.1 | 320 |

As can be seen from the data in Table 7, under normal spinning conditions the number of foreign substances will increase, and toughness will be inferior to that of no. 3, despite still being higher than in conventional articles.

(Effect of the Invention)

In the present invention, it is only by stipulating the polymer catalyst composition, and by specifying the polyester fiber, that rubber-reinforcing original yarns having high toughness as well as good dimensional stability, heat resistance, and durability can be obtained. The original yarns are particularly useful for tire cords, which can be used to produce more-lightweight tires since they will have fewer ends and plies than conventional tires. The good dimensional stability will allow tires with good uniformity to be obtained.

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